

# Substitution of DABCO head group in Polybenzimidazole-crosslinked-PVBC anion exchange membranes (WPEH)

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## 1. Introduction

Anion exchange membranes (AEMs), key component in zero gap alkaline water electrolyzers and fuel cells, have attracted growing interest because of the advantages of alkaline conversion devices [1]. AEMs containing cationic groups (CGs) bounded to a polymer backbone are usually employed. 1,4-diazabicyclo (2.2.2) octane (DABCO), having geometric restrictions unfavorable for hydroxyl attack, was proposed as alternative to poor stable in alkaline media trimethylamine based CGs. Poly[2-2'-(m-phenylene)-5-5'-bibenzimidazole] (PBI), crosslinked with poly(vinylbenzyl chloride) (PVBC) quaternized by DABCO [2] attained an acceptable performance in Hydrogen AEMFC testing. Then, a similar AEM quaternized with BDABCO [3], a N1-butyl substituted doubly charged 1-butyl-4-aza-1-azaniabicyclo [2.2.2] octane bromide, showed improved conductivity.

In this work, we study the quaternization with BDABCO of a previously reported poly(2,5-benzimidazole) (ABPBI)-c-PVBC/OH membrane [4], quaternized with DABCO. Then, we go further in DABCO substitution by alkyl halides, by studying a similar membrane, quaternized with 1-tetradecanyl-4-aza-1-azaniabicyclo [2.2.2] octane bromide (TDABCO).

## 2. Experimentale

### 2.1 Preparation of ABPBI-c-PVBC/CG/OH membranes

ABPBI polymer, averaged  $M_w$  23,200  $\text{g}\cdot\text{mol}^{-1}$ , was synthesized according to a reported procedure [5]. PVBC, 60/40 mix of 3- and 4-isomers average  $M_w$  ~55,000 and ~100,000 respectively, (Sigma Aldrich), and DABCO, 99 wt. %, (Sigma Aldrich), were used as received.

The alkylated DABCO were synthesized from 10.1 g of DABCO dissolved in 100 mL of AcOEt at room temperature, then the corresponding n-alkyl chloride was added in molar ratio of (1:2). After stirring during 16 h, the product was precipitated, washed several times with AcOEt and dried under vacuum.

ABPBI-c-PVBC (ABPBI: PVBC 1:2) were prepared by the casting, from a solution of ABPBI (1 wt. %),  $\text{LiNO}_3$  (1 wt. %) and PVBC (X wt. %) in NMP. The mixture was placed in a Petri dish and dried in an oven at 100 °C for 48 h, with careful control of the temperature and time, in order to reproduce

the crosslinking grade of the membrane.

ABPBI-c-PVBC films were quaternized by immersion in a 0.5 M ethanol solution of the quaternizing agent (DABCO, BADCO or TDABCO) at 60 °C, for 24 h. These membranes were denoted as ABPBI-c-PVBC/CG/Cl. The ABPBI-c-PVBC/CG/Cl films were then converted to the OH<sup>-</sup> form immersing them in a 1M KOH aqueous solution, to obtain the ABPBI-c-PVBC/CG/OH membranes. The preparation pathway is schematized in Fig. 1.

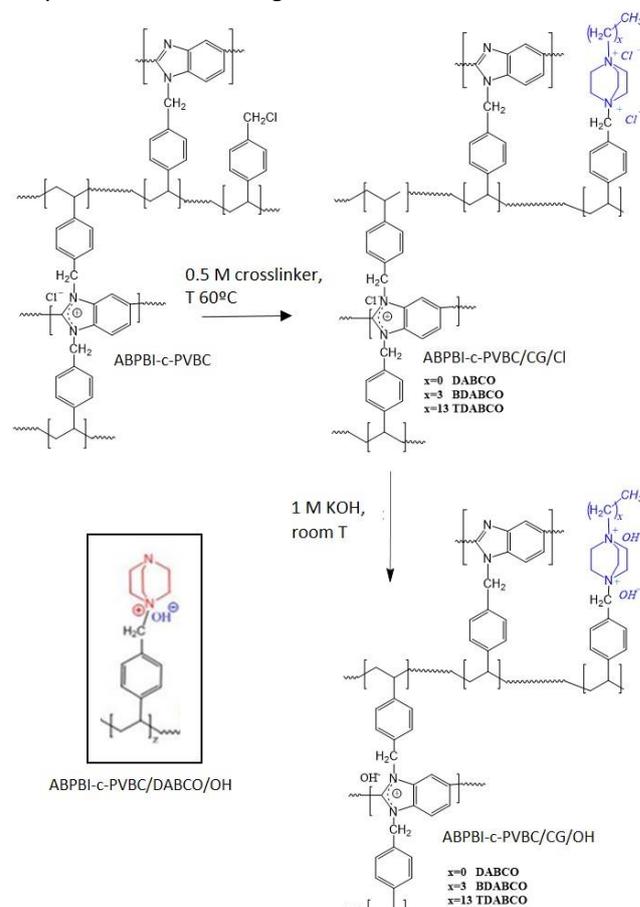


Fig. 1. Preparation pathway of ABPBI-c-PVBC/CG/OH membranes.

### 2.2 Spectroscopic characterization

Proton nuclear magnetic resonance (<sup>1</sup>H NMR) spectra of

BDABCO and TDABCO were done in a Bruker AC 200, employing deuterium chloroform as solvent and TMS as internal standard.

Fourier transform Infrared spectra (FTIR) measurements were taken before and after the quaternization stage of the membranes, by means of a Thermo Scientific Nicolet 6700 FTIR spectrometer.

### 2.3 Ionic exchange capacity and conductivity measurements

For ionic exchange capacity (IEC) determination, membrane samples immersed in 50 mL of 1M NaCl aqueous solution were titrated by means of a Titrette GMBH bottle-top digital burette with aqueous 0.02M H<sub>2</sub>SO<sub>4</sub>, using methyl red reactive as a visual indicator of the end point.

The ionic conductivity ( $\sigma$ ) was measured by means of the impedance method (EIS) in a temperature range between 25°C and 80°C, with an Autolab PGSTAT 30N coupled to a frequency response analyzer (FRA) and a two-point cell composed of two stainless steel plates in contact with both sample faces, as it was previously described [5].

### 2.4 Water electrolysis measurements

The performances of the membranes in a laboratory scale alkaline water electrolyzer of zero gap configuration as reported elsewhere [5] were evaluated. A 1 M KOH aqueous solution was circulated. The current density-potential curves were measured in the 1.5-2.0 V range at 50 °C. In chronopotentiometric measurements, a current density of 200 mA·cm<sup>-2</sup> was applied for 60 min, at 50 °C.

## 3. Results

BDABCO and TDABCO molar yield was 92% and 97% respectively. In Figure 2 is shown <sup>1</sup>H NMR spectrum of BDABCO. It is important to remark that as well as spectra of BDACO and TDABCO, the signal at 2.65 ppm of DABCO, assigned to CH<sub>2</sub> groups adjacent to nitrogen atom, were not observed, indicating a successful substitution of DABCO head group.

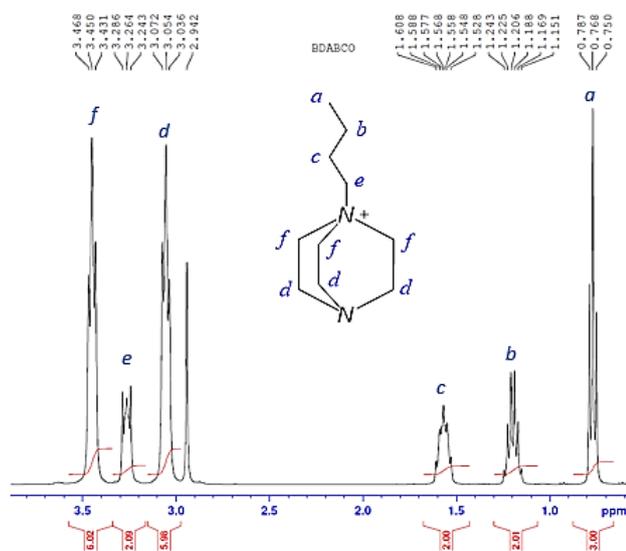


Fig. 2. <sup>1</sup>H NMR spectra of alky BDABCO.

Fig. 3 shows the FTIR spectra of ABPBI and PVBC polymers and crosslinked ABPBI-c-PVBC membranes, before and

after quaternization. The 1267 cm<sup>-1</sup> signal corresponds to the stretching of the -CH<sub>2</sub>Cl group, where quaternization takes place. The 1460 cm<sup>-1</sup> signal can be assigned to the stretching of the quaternary ammonium group, as a result of the quaternization process.

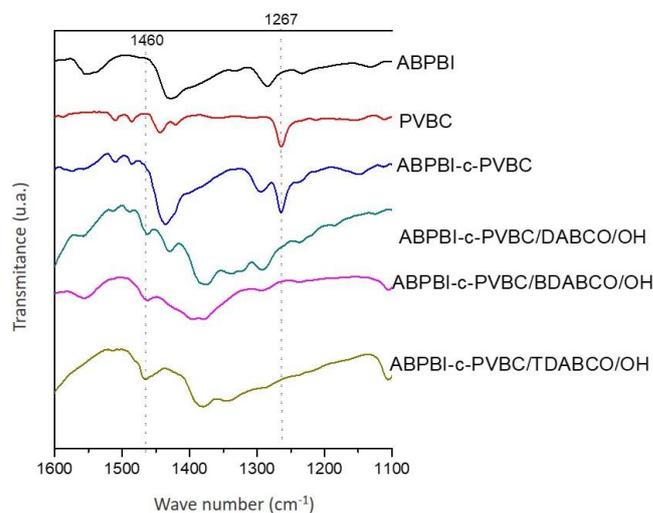


Fig. 3. FTIR spectra of ABPBI-c-PVBC/CG/OH membranes.

The ionic exchange capacity of ABPBI-c-PVBC/CG/OH membranes is shown in Table 1.

Table 1. IEC of ABPBI-c-PVBC/CG/OH membranes.

Membrane	IEC (mmol·g <sup>-1</sup> )
ABPBI-c-PVBC/DABCO/OH	1.70 ± 0.04
ABPBI-c-PVBC/BDABCO/OH	2.13 ± 0.02
ABPBI-c-PVBC/TDABCO/OH	0.82 ± 0.04

Fig. 4 shows the anionic specific conductivity of ABPBI-c-PVBC/CG/OH membranes. Considering the poor performance of ABPBI-c-PVBC/TDABCO/OH membrane, according to IEC and conductivity results, this membrane was not taken in account in alkaline water electrolysis measurements, that are shown in Fig. 5, current potential and chronopotentiometric curves (a) and (b), respectively.

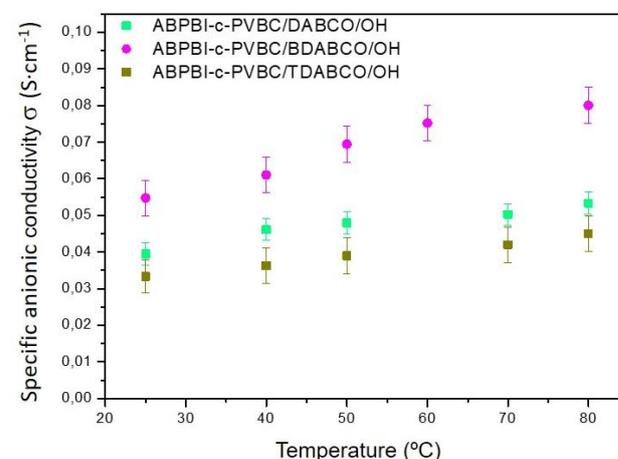


Fig. 4. Ionic conductivity of ABPBI-c-PVBC/CG/OH membranes.

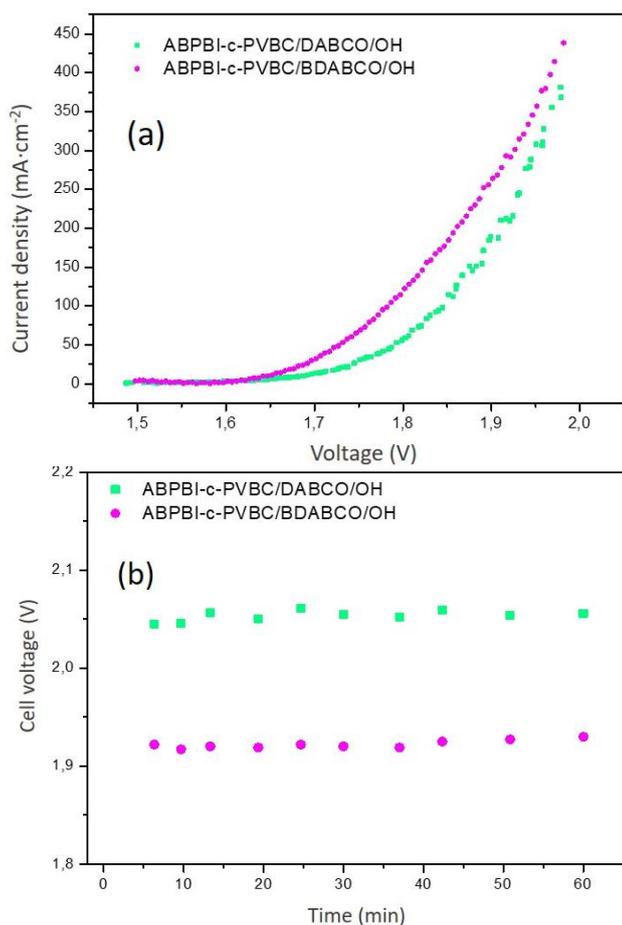


Fig. 5. Water electrolysis of ABPBI-c-PVBC/CG/OH membranes.

#### 4. Discussion

By alkyl halide substitution of the quaternizing agent DABCO, we studied the effect of varying the alkilic chain length, while incorporating an extra cationic group. IEC results show the trend:  $IEC_{BDABCO} > IEC_{DABCO} > IEC_{TDABCO}$ , indicating that the extra CG increases the CG density in BDABCO compared with DABCO membranes, but some factors possible related with the length of the alquidic chain in TDABCO decreases the CG density compared with DABCO, thus cancelling the advantage of adding an extra CG.

The same tendency is observed in conductivity measurements, being  $\sigma_{BDABCO} > \sigma_{DABCO} > \sigma_{TDABCO}$ . Regarding alkaline water electrolyzer measurements, BDABCO membranes show the best performance in current potential curves, with  $430 \text{ mA}\cdot\text{cm}^{-2}$  vs  $370 \text{ mA}\cdot\text{cm}^{-2}$  of DABCO at 1.98 V; and also in chronopotentiometric curves, with 1.93 V vs 2.05 V of DABCO at a fixed current density of  $200 \text{ mA}\cdot\text{cm}^{-2}$ .

#### 5. Conclusions

BDABCO and TDABCO were synthesized with yields higher than 90%, without secondary products or impurities, as demonstrated by  $^1\text{H}$  NMR measurements. The quaternization of ABPBI-c-PVBC membranes with BDABCO and TDABCO was successfully done, as demonstrated by FTIR spectra. The incorporation of an extra CG resulted in higher IEC, conductivity and WE performance of membranes quaternized with BDABCO compared with that quaternized with DABCO. AEMs quaternized with TDABCO showed lower IEC and conductivity than that of AEMs quaternized with

DABCO, possible caused by the excessive length of the alquidic chain, that decreases the CG density, cancelling the advantage of adding an extra CG. The simplicity of DABCO modification would allow to study other routes, varying the alquidic chain length or adding functional groups in order to obtain optimized properties in the resulting AEMs.

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